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Impregnant Composition in Dispenser Cathodes

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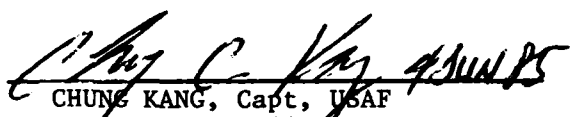**APPROVED FOR PUBLIC RELEASE;
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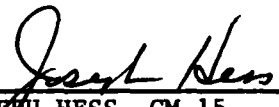P.O. Box 92960, Worldway Postal Center
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20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

The compositions of impregnants inside B-type dispenser cathodes containing barium calcium aluminates were examined by means of quantitative microprobe analysis. The impregnant inside the porous tungsten structure was supported with plastic in order to prevent damage when the cathode was sectioned. The impregnant compositions were found to be consistently deficient in CaO when compared to the nominal composition. Variations and reproducibility in composition are discussed.

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PREFACE

The authors would like to thank S. F. Frederick and Dr. W. J. Hamilton for valuable discussions on sample preparation and analysis, and R. W. Fitzgerald of Diafin Consulting for microprobe analysis.

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I. INTRODUCTION

Because of their inherent ability to emit at high current density, dispenser (impregnated) cathodes are used in traveling-wave tubes in space communication systems, where the reliability and reproducibility of the cathodes are of great importance. The reproducibility of these cathodes can be affected by variations in the composition of impregnants within the cathodes. The impregnant is important because it is the source of the barium needed to obtain a low-work-function surface. The impregnation process is somewhat difficult to control and therefore can contribute to composition variation.

Dispenser cathodes are commonly impregnated by placing the calcined barium calcium aluminate impregnants in contact with the emitting surface of the porous W structure and then heating the assembly past the melting point of the impregnant material, to about 1650°C. All this would be done following a fixed time-temperature schedule during which the W structure is filled by capillary action. Because the filling process is governed by melting kinetics, it is possible that the cathodes are preferentially filled with the lowest viscosity phases, which results in nonuniform composition inside the cathodes. Such incongruent melting, if it should occur, may very well cause the impregnant composition to be quite different from the nominal one and can contribute to a lack of device reproducibility.

Up to now, no direct quantitative measurement of impregnant composition or uniformity inside dispenser cathodes has been reported. This report describes the results of an attempt to perform quantitative measurements on impregnant composition. The technique will be described in some detail because it may be useful in a variety of applications requiring a determination of impregnant compositions inside dispenser cathodes. An electron microprobe was used for pore-by-pore analysis of cathodes sectioned to expose their interiors. A typical sample surface is shown in Fig. 1. An important part of the analysis involves preparing the surface of the specimen without disturbing the impregnant in the pores. A method to achieve this condition is
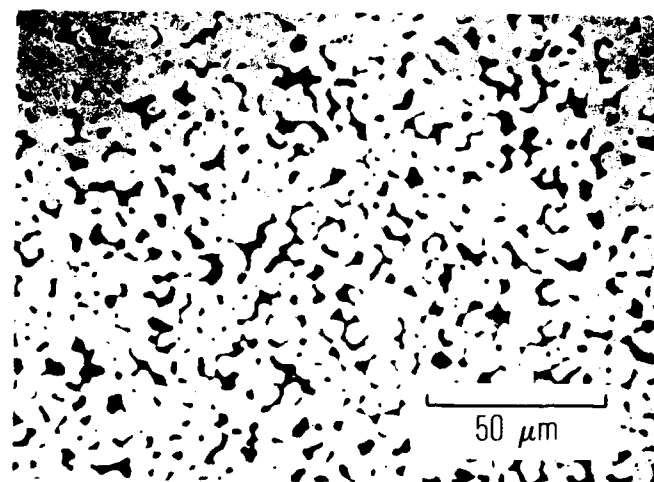
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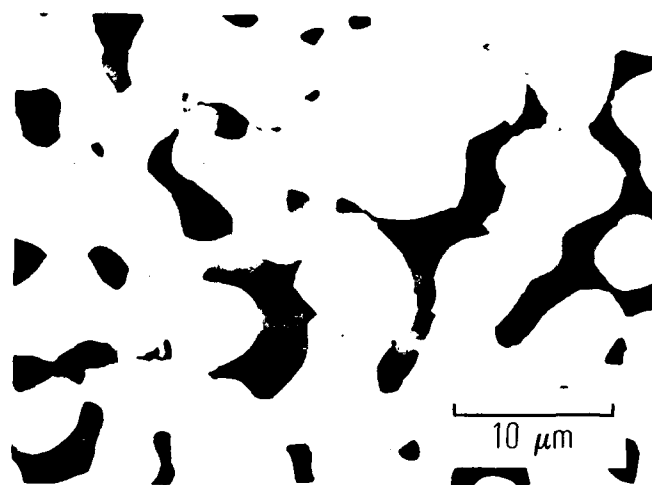
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Fig. 1. (a) SEM Photomicrograph of a Cathode Specimen Surface (Sample
C1) Prepared by the Method Described in the Text. The darker
areas are the pores filled with impregnant materials. (b)
Detail of (a), Showing Undisturbed Impregnant.

described below. The technique is spatially resolved, and therefore will provide information on uniformity of the impregnants. This work is confined to the B cathode, which has the composition $BaO:CaO:Al_2O_3$, in 5:3:2 molar ratios.

II. EXPERIMENTAL PROCEDURE

Sectioned cathodes were analyzed in an electron microprobe (via wave-length dispersive x-ray analysis). This technique was chosen because it is inherently quantitative, has reasonable sensitivity, and has sufficient spatial resolution to analyze materials inside pores.

In order to determine quantitatively the composition of the impregnant, it is first necessary to isolate the impregnant from the W matrix; the impregnant must be analyzed pore by pore, by directing the beam at a point away from the W wall. A second requirement for obtaining quantitative results is a flat and smooth sample surface. However, an impregnated cathode by its nature presents a special problem in sample preparation, as the impregnant material of interest is held loosely in the pore network of W. On a sectioned surface, the exposed pores are irregular in shape, and are typically a few micrometers on the side. Polishing such a porous structure directly would result in smearing and loss of the impregnant material. Thus in our work the entire structure was first infiltrated with plastic in order to hold the impregnants in place. The cathodes were then polished lengthwise to yield a smooth sample surface. Careful examination by scanning electron microscopy (SEM), and an analysis of aged cathodes (to be reported elsewhere) for which there are expected systematic compositional profiles, indicate that sample preparation causes no detectable smearing of impregnant materials. The procedure for preparing samples is described below.

The samples were placed in glass vials and rough-pumped in a glass chamber equipped with a hopper attachment. Then a mixture of monomethyl methacrylate (40 cm^3), dried benzoyl peroxide (0.3 g), and dimethylanaline (0.16 cm^3) was dropped over the samples. After a few more minutes of pumping, the chamber was backfilled with dry nitrogen and the vials were capped and left to stand at room temperature until the polymerization process was complete (typically 24 hr). Sections of the plastic containing the samples were then removed, mounted in epoxy, and polished successively with 240-, 400-, and 600- grit silicon-carbide paper, with kerosene as a lubricant to

minimize the reaction of the impregnants with water. For final polishing, a Syntron model LP010 vibration polisher with a short-napped silk cloth charged with 1-µm diamond paste lubricated with kerosene was used. The 1-in. mounted samples were weighted by 120-g sample holders and polished for 3 hr at full speed. The samples were cleaned ultrasonically with Freon TF as the solvent and were stored in a vacuum dessicator. As an alternative, we have used a Buehler Minimet polisher with a nylon cloth, 1/4-µm diamond paste, and kerosene lubricant. The load was set at minimum and the speed at 5; the final polishing time was several hours. The polished samples were coated with carbon to prevent them from being charged by the electron beam during analysis.

Microprobe analyses were done under the conditions given in Table 1. B cathodes from four sources were analyzed. The cathodes were either unused or had been activated (via heating for about 30 min at 1200°C brightness temperature) and operated at a typical operating temperature of 1050°C brightness for up to 300 hr. For such a short operating time, there was no observable systematic difference in composition. If one were to examine the cathodes within a few micrometers the emitting surface, some compositional change might be seen. However, here we are primarily concerned with systematic variation in the entire interior of the cathodes, which were about 1000 µm thick. The short operating time apparently did not introduce any systematic change in composition.

The precision of the instrument was better than 1%, as judged by the results when the beam was repeatedly directed to the same spot. To characterize a cathode, 20 to 60 pores were analyzed.

Measurements were made with two results in mind: (1) to determine the average composition and its standard deviation within each cathode, and (2) to investigate the potential and systematic variation of composition as a function of distance from the emitting surface. Thus, several pores were analyzed in bands at the same distance from the surface; several bands at various distances from the surface provided a depth profile.

Table 1. Experimental Conditions of Electron
Microprobe Analysis

Analyzed Element	Standard	Spectrometer Crystal	Analyzed Line
Ba	$BaSO_4$	PET	L_α
Ca	$CaSiO_3$	PET	K_α
Al	Al_2O_3	TAP	K_α
W	W	TAP	M_α

Instrument: Cameca Camebax-Micro electron microprobe

Accelerating voltage and beam current: 15 kV, 8 nA

Beam size: ~0.2 μm

Analysis program: Cameca adaptation of COR 2

Counting time: 30 sec for peaks, 15 sec for background

The greatest concern about the ability to analyze impregnant composition was caused by the presence of W. A typical correction program compares the measured individual signals of the selected elements against those of the standard samples to yield a set of concentrations which serves as an input to an interactive program. This program corrects for different excitations as a function of atomic number, self absorption, and x-ray fluorescence in order to seek a final composition that is most consistent with the set of measured intensities. Thus, significant extraneous signals from the W wall would give erroneous results because the correction program assumes that W is present uniformly in the excitation volume. In practice, the extremely small pores were avoided because the excitation volume was estimated to resemble roughly a sphere having a volume of 1 μm^3 (for greater details, see Ref. 1). Therefore the "necked-down" regions of the pore network were not sampled, but those pores sampled represent practically all the materials present inside the cathodes.

III. RESULTS AND DISCUSSION

The selected elements for analysis were Ba, Ca, Al, and W. W signals can come about from excitation of the W matrix or from tungstates. Tungstates have traditionally been considered to be a potential product formed during impregnation. Tungstate formation must be minimized by rapidly cooling the cathode as soon as impregnation is thought to be complete. The electron microprobe, of course, is not capable of distinguishing the various forms of W. In our analysis, a thin layer (less than 1 μm) of tungstate formed against the wall cannot be detected because the tungstate signal is not distinguishable from that caused by the excitation of the W wall. In relatively large pores, it is possible to map out the intensity of the W signal as one scans across the pore. The result is what one would expect: a high W signal outside the pore and an essentially W-free signal in the impregnated pores. The data taken were not sufficient to determine if there was a systematic variation of Ba, Ca, or Al inside the pores.

The results of an analysis, as given by the correction program described earlier, are given in weight percent. These results are not normalized; that is, the total weight need not be exactly 100% because the criterion was to obtain a set of concentration values most consistent with the measured intensities. Our results of summing the four elements – Ba, Ca, and Al as oxides and W as a metal – were between 96.7 and 99.7%, indicating that the samples contain closely the elements selected for analysis and that the excitation volumes were quite homogeneous. When the sample was not properly prepared and contained large amounts of water, the unnormalized weights would add up to from 70 to 80%, instead of close to 100%. Similarly, if the W signal is very large (~10%), as when the beam irradiates the wall or when the impregnant is suspected to be very thin, the total unnormalized weight would vary from 60 to 80%. In the data shown below, about half of the pores showed no measurable W (less than 0.01%) and in all samples the average W concentration was less than 0.5% by weight, giving us confidence that the measurement technique is quite free of W-matrix interference and is capable of yielding quantitative results of impregnant composition.

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The compositions of seven samples in unnormalized weight percent are shown in Table 2, which also shows the number of pores analyzed in each sample.

Table 3 presents the same results in the more familiar unit of mole percent. In this case, W concentration is ignored and the concentrations of Ba, Ca, and Al are normalized to 100%. Several observations can be made:

(1) The measured composition is quite different from the nominal $BaO:CaO:Al_2O_3$ composition of 5:3:2. The greatest difference is in CaO, which is found to be deficient and results in a correspondingly higher concentration of Al_2O_3. The average measured concentration of $BaO:CaO:Al_2O_3$ is 5:2.2:2.3.

(2) Within this relatively small sampling, all the cathodes are quite uniform, as evidenced by the small standard deviation values in all cases. The element least uniformly distributed is Ca.

(3) There is remarkably little difference among various sources; the compositions agree to within one standard deviation.

The variation of composition within sample B1 is shown in the phase diagram (Ref. 2) in Fig. 2. It is deficient in Ca, which also has the greatest variation in concentration. The vapor pressure of BaO in these formulations and also their ability to generate Ba by reacting with W is estimated to be very similar to the nominal 5:3:2, because of the existence of a range of solid solutions in this area of the phase diagram.

The dependence of composition on position was studied in only two samples. The motivation, of course, was to find evidence for the suspected phase segregation that may occur during impregnation. The results of a compositional profile as a function of distance from the emitting (and also the impregnating) surface are shown in Fig. 3. The variation is not expected to be large, given the observed uniformity implied in Table 1. One may possibly interpret Fig. 3 as indicating some systematic variation with depth on the concentration of CaO and Al_2O_3, but that variation, even if it is real, is not large.

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Table 2. Results of Impregnant Analyses
(Unnormalized Concentration, Weight %)

Samples	No. Pores Measured	BaO	CaO	Al_2O_3	W
A1	38	66.8 ± 2.2	10.8 ± 1.7	22.6 ± 1.4	0.69 ± 0.66
A2	20	67.7 ± 1.4	10.9 ± 1.7	22.1 ± 0.6	0.32 ± 0.23
B1	50	67.6 ± 1.5	11.0 ± 2.1	20.5 ± 1.0	0.30 ± 0.50
B2	19	67.5 ± 2.1	11.0 ± 2.8	20.5 ± 1.2	0.94 ± 0.65
C1	60	66.7 ± 1.7	10.7 ± 1.5	19.2 ± 1.1	0.18 ± 0.45
D1	40	67.8 ± 2.5	10.0 ± 2.8	20.7 ± 1.0	0.49 ± 0.68

Note: A, B, C, and D designate four suppliers. Samples A1 and B2 were activated only; A2 was activated and burned for approximately 300 hr at 1050°C. The remainder were unused.

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Table 3. Results of Impregnant Analyses
(Normalized Concentration, Molar %)

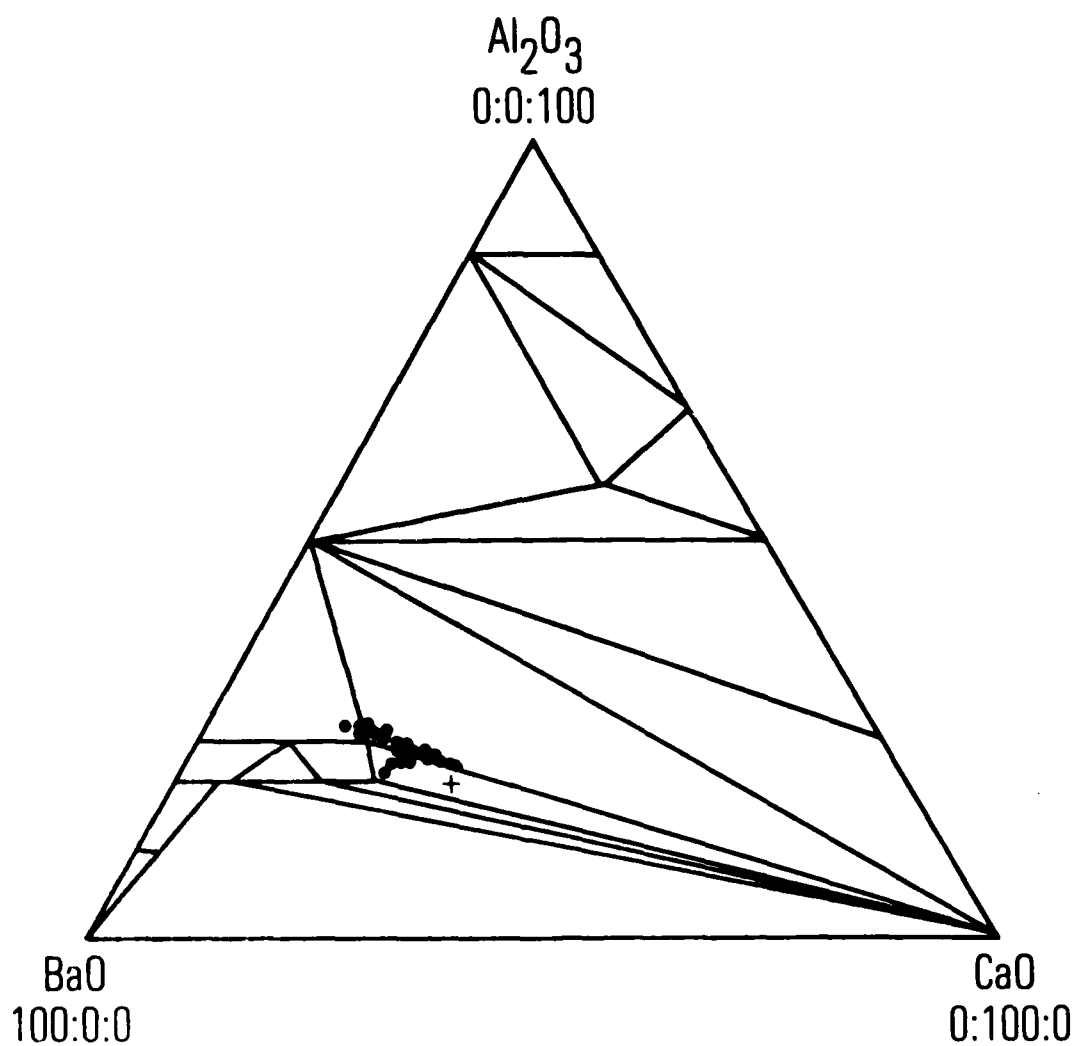| Samples	No. Pores Measured	BaO	CaO	Al_2O_3
A1	38	51.2 ± 2.5	22.7 ± 3.1	26.1 ± 1.6
A2	20	51.8 ± 2.0	22.8 ± 3.0	25.5 ± 1.1
B1	50	52.7 ± 2.5	23.2 ± 3.8	24.1 ± 1.6
B2	19	52.7 ± 3.3	23.3 ± 5.0	24.1 ± 2.0
C1	60	53.5 ± 2.2	23.3 ± 2.8	23.2 ± 1.4
D1	40	53.7 ± 3.4	21.6 ± 5.2	24.7 ± 1.8

Fig. 2.   Phase Diagram for the BaO:CaO:Al₂O₃ System at 1250°C
          (Ref. 2).   Data points are for sample Bl; nominal composition
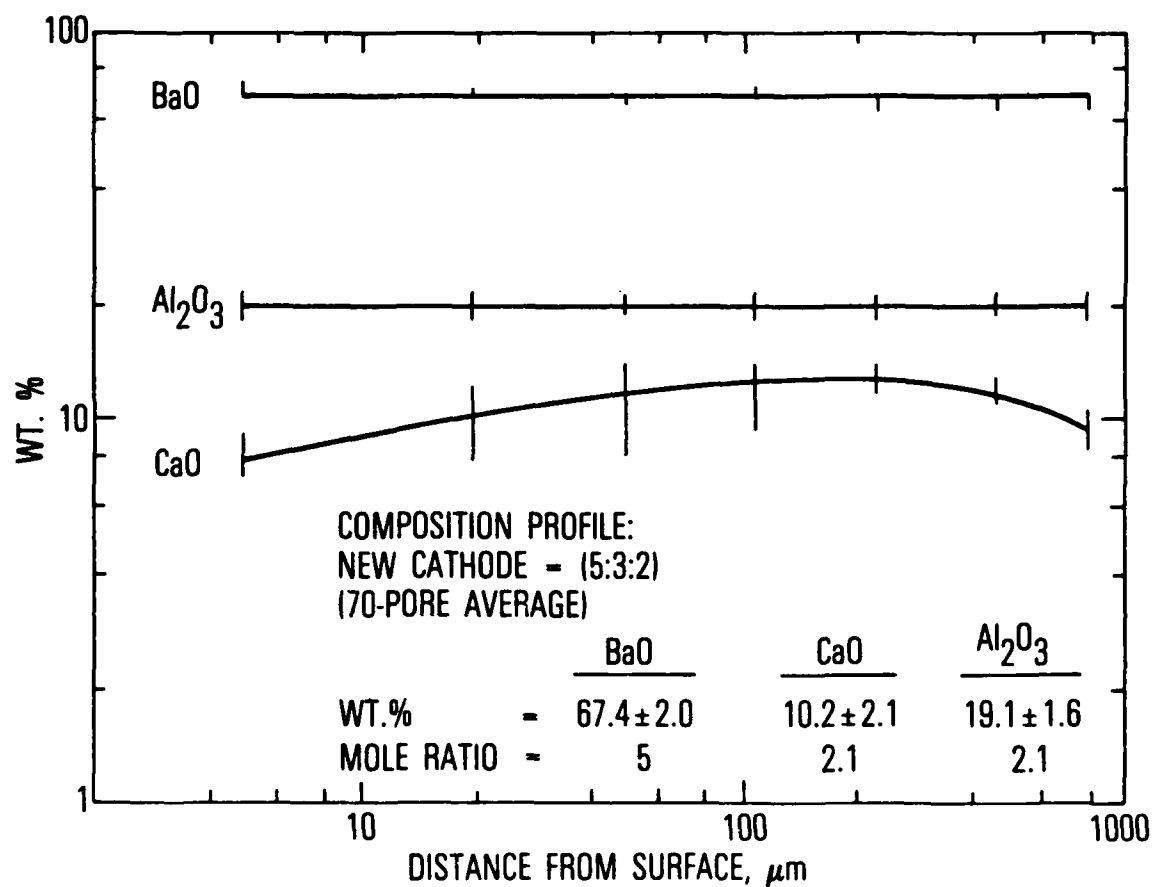   (5:3:2) is indicated by "+".

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Fig. 3. Composition Profile of a New Cathode, Sample B1. The vertical
bars show the standard deviation obtained from measurements of
ten pores at each position.

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IV. CONCLUSION

A technique has been developed to analyze the composition of impregnants inside dispenser cathodes. It can be applied to monitor the consistency of production procedure and to check the reproducibility of the device. The technique can be adapted to analyze similar systems where materials are imbedded in a porous matrix.

Based on limited sampling, the nominal composition in B cathodes was not observed. Instead we found an impregnant deficient in CaO. However, cathode operation may not be drastically affected because the thermodynamic properties of the calcium-deficient impregnant may be quite similar to the nominal $BaO:CaO:Al_2O_3$ composition of 5:3:2 in B cathodes because of the existence of solid solutions in this general compositional range. Additional investigations, however, are needed before this conclusion can be considered firm. The general problem of selecting impregnants to meet specific applications can be approached by using this technique in conjunction with the phase diagram and thermodynamics. The uniformity of impregnant compositions within cathodes and among suppliers was very good. The results show a far more uniform and reproducible impregnant composition than many investigators had previously thought. The sampling here is small, and the good uniformity can be construed as what can be obtained, rather than as a statistical representation of a large population of commercial cathodes. The true composition in cathodes containing other nominal formulations, such as 4:1:1, is not known. Similarly, the detection of tungstates formed during impregnation will require further investigation.

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